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## Baseline

## Monitoring of a wide range of organic micropollutants on the Portuguese coast using plastic resin pellets

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## ABSTRACT

We analyzed polychlorinated biphenyls (PCBs), dichlorodiphenyl dichloroethane and its metabolites, hexachlorocyclohexanes (HCHs), polycyclic aromatic hydrocarbons (PAHs), and hopanes, in plastic resin pellets collected from nine locations along the Portuguese coast. Concentrations of a sum of 13 PCBs were one order of magnitude higher in two major cities (Porto: 307 ng/g-pellet; Lisboa: 273 ng/g-pellet) than in the seven rural sites. Lower chlorinated congeners were more abundant in the rural sites than in the cities, suggesting atmospheric dispersion. At most of the locations, PAH concentrations (sum of 33 PAH species) were ~100 to ~300 ng/g-pellet; however, three orders of magnitude higher concentrations of PAHs, with a petrogenic signature, were detected at a small city (Sines). Hopanes were detected in the pellets at all locations. This study demonstrated that multiple sample locations, including locations in both urban and remote areas, are necessary for country-scale pellet watch.

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## 1. Introduction

International Pellet Watch (IPW) is globally monitoring persistent organic pollutants (POPs) by using plastic resin pellets. Plastic resin pellets are small granules, generally in the shape of a cylinder or disk with a diameter of a few millimeters. These plastic particles are the industrial feedstock of plastic products. A small portion of them are spilled into the environment during land handling and transport. Because polyethylene (PE) pellets, a major type of plastics, are lighter than water, such spilled PE pellets are carried by surface runoff, streams and rivers, and finally reach the ocean. Because of their persistent nature, such pellets are distributed all over the world. Hydrophobic organic pollutants are sorbed into and concentrated in the pellets from surrounding sea water (Mato et al., 2001). Meanwhile, the importance of global monitoring of POPs has been emphasized in the Stockholm Convention (UNEP, 2001). Thus, we initiated the IPW in 2005 (Takada, 2006). The advantage of the IPW method is its extremely low sampling and shipment cost, in comparison to conventional monitoring using

water, sediment and biological samples. In our previous study (Ogata et al., 2009), we examined the utility of the IPW method as a means of global monitoring, by comparing it with mussel monitoring. Polychlorinated biphenyl (PCB) concentrations in pellets correlated well with those in mussel from the same area, indicating the reliability of the IPW method as a global monitoring technique.

Our previous paper (Ogata et al., 2009) elucidated the spatial pattern of POPs in 17 countries. However, for most of the countries, only a few locations were investigated and thus the calculated pollution levels for the countries may have been inaccurate. For example, only one location (Kato Achaia), a remote area, was available in Greece in the first report (Ogata et al., 2009), and showed the lowest PCB concentration (5 ng/g-pellet) in the world. However, our follow-up study (Karapanagioti et al., 2011), based on four locations in Greece, revealed two orders of magnitude higher concentrations of PCBs (230 and 260 ng/g-pellet) in two locations near the capital, Athens, a highly industrialized area. Similarly, the first report of the IPW (Ogata et al., 2009) sampled only one, remote location in Portugal (Aveiro), suggesting a possible underestimation of POP contamination levels in Portugal. Thus, here we added pellet samples from eight locations on the Portuguese coast to obtain a more detailed assessment of the pollution levels in Portugal,

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based on the 9-pellet sample. Furthermore, in the previous, country-wide study in Greece, urban and remote locations were hydrologically distinguished due to the complex geographical setting (thousands of islands and peninsulas). In contrast, in the present study, all the sample locations were on the same coastline, facing the Atlantic Ocean, within 50–100 km of each other. This provided an opportunity to enhance both our understanding of pellet-sample location selection, and discussion of the behavior of POPs.

In addition, the present study analyzed 33 polycyclic aromatic hydrocarbons (PAHs), including methyl PAHs and hopanes, in pellets, as new target compounds for the IPW. PAHs are introduced to the marine environment via petroleum pollution, in addition to inputs of combustion products of organic matter (e.g., fossil fuel, biomass). Because of their toxicity, PAHs have been monitored in seawater, sediments, and biota. However, there has been only two reports on PAHs in pellets (Karapanagioti et al., 2011 and Van et al., 2012). In these study the number of PAH species was rather limited (18 species). The present study increased the number of target compounds up to 33. Hopanes, pentacyclic triterpanes, are contained in crude oil and some refined petroleum products such as lubricating oil and asphalt. Hopanes are source-specific and persistent to a variety of environmental alterations (microbial and photolytic degradation), and therefore have been used as petroleum biomarkers. PAHs and hopanes in pellets can thus be used as markers of petroleum pollution in the IPW. However, no detailed investigation has been conducted on the utility of these compounds.

The present study conducted detailed-scale monitoring of POPs (i.e., PCBs, DDTs, and HCHs), PAHs, and hopanes, in pellets collected from nine locations on the Atlantic coast of Portugal. In terms of IPW protocol, the present study provided (1) further information on the selection of sampling locations in respective countries, and (2) preliminary evaluation of hopanes as markers of petroleum pollution.

## 2. Materials and methods

Plastic resin pellets from eight Portuguese beaches were collected in 2008 and 2012 (Fig. 1). In addition, the analytical results

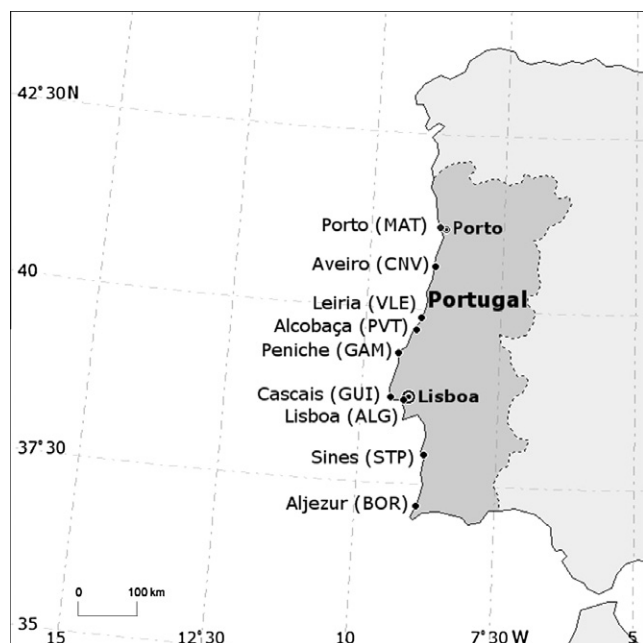


Fig. 1. Sampling locations of resin pellets.

on pellets from Aveiro, where POP concentrations had been reported in our previous study (Ogata et al., 2009), were included in the present study. Among the total of nine locations, Lisboa and Porto are large cities in Portugal, with Lisboa the capital and Porto the second-largest city. The other seven locations are in rural areas. More detailed information, including the coordinates of the sampling locations, is listed in Table 1, where the nine locations are listed in latitudinal order from north to south (illustrated in Fig. 1). Pellets were sorted and POPs analyzed as in Ogata et al. (2009). Pellets were sorted with a near-infrared spectrometer (Plascan-WTM OPT Research Inc., Tokyo, Japan) into polyethylene (PE), polypropylene (PP), and other polymers. Yellowing PE pellets (with a yellowness of  $\geq 40$ ) were selected for chemical analysis. Median POP values were obtained by analyzing 5 pools of pellets (each pool consisting of five randomly selected pellets) from each location.

POPs were extracted from pellets by soaking the pellets in hexane. The extracts were separated through fully activated silica gel columns into three fractions: Fraction I (*n*-alkanes and hopanes), Fraction II (PCBs and DDE), and Fraction III (DDT, DDD, 4 HCH isomers [ $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ], and polycyclic aromatic hydrocarbons [PAHs]). The hopanes in Fraction I were determined by gas chromatography/mass spectrometry (GC–MS). The PCBs and *p,p'*-DDE in Fraction II were determined by gas chromatography/ion-trap mass spectrometry. The sum of all the quantified congeners (i.e., CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206) is expressed as  $\sum 13$  PCBs. The *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD and the four HCH isomers in Fraction III were determined by gas chromatography/electron capture detection. The PAHs in Fraction III were quantified by GC–MS. The sum of all 33 quantified PAH species is expressed as  $\sum 33$  PAHs. The instrumental conditions for the organochlorine compounds are described in Ogata et al. (2009), and those for the hopanes and PAHs in Saha et al. (2009). No recovery correction was applied to any components, except for the PAHs, because good recoveries had been confirmed prior to the sample analysis. PAH concentrations in the samples were recovery-corrected using recoveries of surrogates (i.e., deuterated PAHs) spiked before analysis, as described in Saha et al. (2009). The reproducibility of this analytical procedure (i.e., column chromatography and instrumental determination) was confirmed by analysis of four aliquots from a single extract of pellets from Buenos Aires, Argentina, for PCBs, DDTs and HCHs; and an extract from Tokyo Bay for PAHs and hopanes. The relative standard deviations of the concentrations were less than 14% for PCBs, DDTs, and HCHs, and less than 10% for PAHs and hopanes. Recovery was tested by spiking the aliquots of the extracts with authentic standards; recoveries were  $>95\%$  for PCBs, DDTs, and HCHs, and  $>74\%$  for PAHs and hopanes. A procedural blank using only solvent was run with every set analyzed (5 pools). Analytical values  $<3\times$  the corresponding blanks were considered below the limit of quantification (LOQ). The LOQs were normally 0.07 ng/g-pellet for  $\sum 13$  PCBs, 0.1 ng/g-pellet for DDT, 0.04 ng/g-pellet for DDE, 0.07 ng/g-pellet for DDD, 0.4 ng/g-pellet for HCHs, 4 ng/g-pellet for total hopanes and 50 ng/g-pellet for  $\sum 33$  PAHs.

## 3. Results and discussion

The analytical results of POPs in all the pellets are listed in Table 2 and Table S1. Table 2 shows the median concentrations of POPs from 5 pools from nine locations on the Portuguese coast. PCB concentrations ranged from 10.5 to 307 ng/g-pellet. PCB concentrations in the two major cities, Porto (307 ng/g-pellet) and Lisboa (273 ng/g-pellet), were one order of magnitude higher than in the rural areas (10.5–41.7 ng/g; Fig. 2). This is consistent with the monitoring of PCBs using sediments (Castro and Vale, 1995), where concentrations of PCBs in sediments from the Tagus estuary in

**Table 1**

Sample information of resin pellets from Portugal.

City name	Beach name	Abbreviation	Latitude			Longitude			
			Degree	Minute	Second	Degree	Minute	Second	
Porto	Matosinhos	MAT	N	41	10	46	W	8	41
Aveiro	Costa Nova	CNV	N	40	37	6	W	8	45
Leiria	Vieira de Leiria	VLE	N	39	52	27	W	8	58
Alcobaça	Alcobaça	PVT	N	39	42	10	W	9	2
Peniche	Gamboa	GAM	N	39	21	53	W	9	22
Cascais	Guincho	GUI	N	38	43	48	W	9	28
Lisboa	Algés	ALG	N	38	41	43	W	9	13
Sines	São Torpes	STP	N	37	55	23	W	8	48
Aljezur	Bordeira	BOR	N	37	11	50	W	8	54

**Table 2**

Median concentrations of POPs (ng/g-pellet) in plastic resin pellets from Portugal coast.

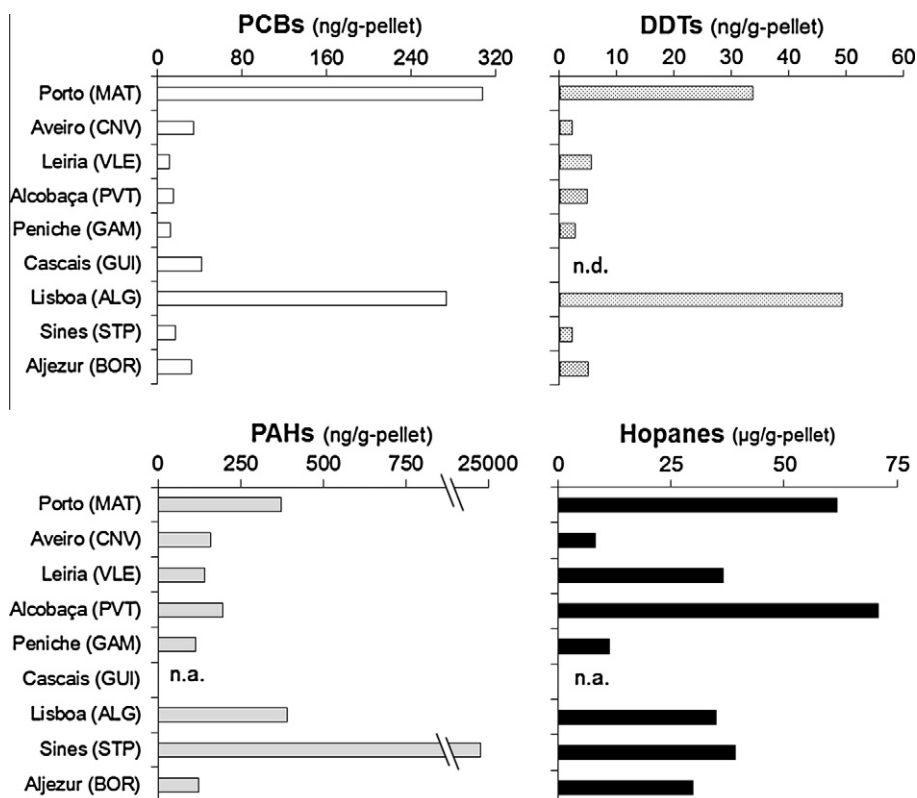
	Porto (MAT)	Aveiro (CNV)	Leiria (VLE)	Alcobaça (PVT)	Peniche (GAM)	Cascais (GUI)	Lisboa (ALG)	Sines (STP)	Aljezur (BOR)
<i>PCBs</i>									
CB-66	0.53	0.067	0.10	0.16	0.11	0.20	0.47	0.12	0.019
CB-101	2.3	0.29	0.43	0.66	0.48	0.73	1.3	0.45	0.16
CB-110	11	2.1	0.71	1.5	0.71	2.1	4.9	0.80	0.60
CB-118	1.7	0.64	0.25	0.31	0.29	0.71	1.0	0.32	0.072
CB-105	0.94	0.53	0.21	0.38	0.21	0.054	0.34	0.12	0.12
CB-149	45	0.85	1.3	2.0	1.6	6.7	33	2.3	2.3
CB-153	41	6.1	1.8	2.5	2.1	5.7	11	1.2	3.3
CB-138	66	12	3.2	3.9	3.6	12	63	6.3	18
CB-128	7.8	1.2	0.32	0.61	0.31	1.4	9.9	0.40	0.54
CB-187	30	2.1	0.83	1.1	0.93	3.5	40	1.8	1.4
CB-180	55	4.6	1.0	1.1	1.1	5.9	68	2.1	3.2
CB-170	44	3.4	0.76	0.41	0.86	3.2	39	1.3	2.5
CB-206	1.3	0.0095	0.0	0.0	0.0	0.017	2.8	0.0	0.0
Σ13 PCBs	310	34	10	15	12	42	270	17	32
<i>DDTs</i>									
pp' DDT	18	1.3	1.7	2.7	0.88	1.0	29	3.7	2.9
op' DDT	2.0	0.38	0.72	0.76	0.54	0.12	2.8	1.8	0.66
pp' DDD	2.8	0.24	1.0	0.64	0.66	0.11	4.0	0.0	0.89
op' DDD	1.4	0.10	1.5	0.0	1.4	0.37	0.89	1.1	0.22
pp' DDE	9.9	0.14	0.65	0.70	0.048	0.39	13	0.45	0.54
Total DDTs	34	2.2	5.5	4.8	2.7	0.0	49	2.3	4.9
<i>HCHs</i>									
αHCH	0.0	0.088	0.0	0.22	0.0	0.13	0.0	0.0	0.35
βHCH	0.0	0.0	0.0	0.38	0.0	0.25	0.0	0.0	0.57
γHCH	0.0	0.46	0.0	0.37	0.0	1.2	0.0	0.0	0.47
δHCH	0.0	0.0	0.0	0.86	0.0	0.23	0.0	0.0	2.0
Total HCHs	0.0	0.55	0.0	0.86	0.0	0.0	0.0	0.0	3.3

Below LOQ mentioned in italic.

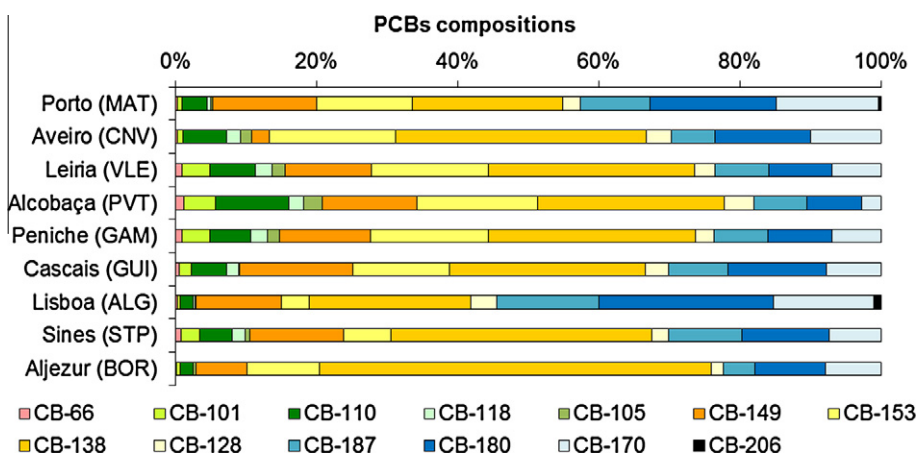
Lisboa were higher than the other two sites in Portugal. PCB concentrations in Porto and Lisboa were comparable to those observed in the other industrial countries discussed in our previous study (Ogata et al., 2009). In that study, Aveiro was the only location in Portugal. However, in the present study, PCB concentrations in pellets from Aveiro were much lower than in those from the two major cities, showing that Ogata et al. (2009) underestimated the pollution levels in Portugal. To ensure unbiased monitoring, multiple locations in respective countries, including locations in both urban and remote areas, should be sampled.

Fig. 3 shows the composition of PCBs in pellets from the Portuguese coast. The composition differed between the urban and rural areas. In the urban locations (Porto and Lisboa), higher chlorinated biphenyls were more abundant, whereas lower chlorinated congeners were more abundant in the remote areas. In pellets from Lisboa, hepta-chlorinated PCBs (CB187, CB180, and CB 170) were predominant (53.5% of the total PCBs). In pellets from Porto as well, hepta-chlorinated PCBs accounted for more than 40% of the total

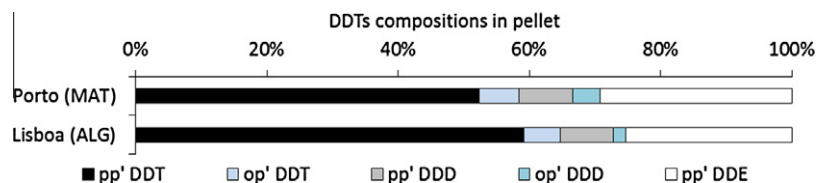
PCBs. On the other hand, the percentages of hepta-chlorinated PCBs in pellets from rural cities were less than 30%. These differences can be explained by differing routes of PCB input to the coastal waters. In the two cities (Porto and Lisboa), which had high PCB concentrations, PCBs in pellets could be derived from legacy pollution, which was introduced to the water body via direct and/or nearby inputs in the past, and accumulated in bottom sediments in the coastal waters. This would then be resuspended and dissolved, contaminating the overlying water; and the PCB composition of these coastal water pellets would thus reflect that found in the respective inputs. On the other hand, in the remote sites, atmospherically-transported PCBs could be the major inputs. Because of the more volatile nature of lower chlorinated congeners in comparison to higher chlorinated congeners, such lower chlorinated congeners could be preferentially transported through the air. This could be the reason why lower chlorinated biphenyls were more predominant in the pellets from remote areas.



**Fig. 2.** PCB, DDTs, PAH and hopane concentrations in pellets from Portuguese coast. PCBs: sum of 13 congeners; DDTs: sum of 5 compounds; PAHs: sum of 33 compounds; Hopanes: sum of 18 compounds.



**Fig. 3.** PCB compositions in pellets from Portuguese coast.



**Fig. 4.** DDT compositions in pellets from coasts in Porto and Lisboa.

The concentrations of DDTs in the respective locations are shown in Fig. 2 and Table 2, and elevated concentrations of DDTs are noted in the two major cities, as in the case of PCBs. The concentrations (33.7 ng/g in Porto, and 49.4 ng/g in Lisboa) are similar

to those in Turkey, Thailand, one Greek city, and some South African cities (Ogata et al., 2009; Ryan et al., 2012). Relative compositions of DDTs for these two locations are shown in Fig. 4. Typically, technical DDTs are composed of 77.1% p,p'-DDT, 14.9% o,p'-DDT, 4%

**Table 3**

Median concentrations of PAHs (ng/g-pellet) in plastic resin pellets from Portugal coast.

	Porto (MAT)	Aveiro (CNV)	Leiria (VLE)	Alcobaça (PVT)	Peniche (GAM)	Cascais (GUI)	Lisboa (ALG)	Sines (STP)	Aljezur (BOR)
Phenanthrene	87	66	38	90	18	n.a.	43	4100	28
Anthracene	30	6.1	2.8	3.4	0.0	n.a.	7.1	100	2.9
CPP	6.9	0.94	1.6	5.2	0.0	n.a.	2.6	260	1.1
3-Methylphenanthrene	17	19	5.6	7.2	8.0	n.a.	7.8	5100	2.1
2-Methylphenanthrene	38	23	11	16	12	n.a.	13	7000	4.1
9-Methylphenanthrene	8.8	14	6.2	6.9	6.5	n.a.	8.4	3500	2.9
1-Methylphenanthrene	14	12	8.1	12	7.0	n.a.	12	3100	4.3
Fluoranthene	19	4.5	5.5	12	2.3	n.a.	12	320	8.2
Pyrene	14	4.7	2.0	4.8	1.4	n.a.	8.8	530	5.7
a-Methylpyrene	2.2	n.a.	4.6	5.4	4.5	n.a.	1.0	59	4.1
b-Methylpyrene	0.0	n.a.	0.0	0.0	2.3	n.a.	1.3	83	0.0
c-Methylpyrene	0.0	n.a.	0.91	0.75	1.1	n.a.	1.3	80	2.5
d-Methylpyrene	0.1	n.a.	0.0	0.0	0.0	n.a.	0.78	46	3.3
Benz[a]anthracene	4.4	0.0	4.0	4.9	4.3	n.a.	3.8	4.4	4.1
Chrysene	24	3.9	16	6.3	3.7	n.a.	9.2	46	8.5
e-Methylchrysene	35	n.a.	0.0	0.0	0.0	n.a.	4.9	0.54	0.0
f-Methylchrysene	5.0	n.a.	19	8.9	11	n.a.	3.2	24	9.6
g-Methylchrysene	3.1	n.a.	0.0	0.0	2.0	n.a.	4.1	3.1	1.9
h-Methylchrysene	1.8	n.a.	0.0	0.68	0.0	n.a.	2.9	0.58	0.0
i-Methylchrysene	3.5	n.a.	0.0	0.69	0.87	n.a.	4.3	3.7	3.8
Benzo[b]fluoranthene	4.8	0.0	0.0	0.95	0.40	n.a.	4.6	1.0	4.4
Benzo[fluoranthene]	2.5	0.0	4.5	3.8	3.1	n.a.	4.9	2.3	0.0
Benzo[e]pyrene	8.4	0.34	0.0	1.1	0.71	n.a.	22	2.0	6.6
Benzo[a]pyrene	2.7	0.0	0.0	0.6	0.78	n.a.	7.2	1.4	2.1
Perylene	1.9	0.0	0.50	0.0	0.80	n.a.	17	0.46	1.5
Indenopyrene	26	4.2	8.5	3.2	20	n.a.	110	5.6	4.7
Benzo[ghi]perylene	3.7	0.58	0.56	0.76	0.73	n.a.	59	2.6	4.7
Coronene	5.6	0.0	0.0	0.0	0.0	n.a.	11	0.0	1.9
Total PAHs	370	88	61	160	50	n.a.	310	24000	53
MP/P	0.90	1.0	0.81	0.46	1.8	n.a.	0.94	4.5	0.48
MPy/Py	0.16	n.a.	2.7	1.3	5.7	n.a.	0.50	0.51	1.7
MC/C	2.0	n.a.	1.1	1.6	3.7	n.a.	2.1	0.69	1.8
MPAHs/PAHs	0.53	n.a.	0.65	0.43	0.97	n.a.	0.20	3.5	0.46

n.a.= not analyzed. Below LOQ mentioned in italic.

**Table 4**

Hopane concentrations (ng/g-pellet) in plastic resin pellets from Portugal coast

	Porto (MAT)	Aveiro (CNV)	Leiria (VLE)	Alcobaça (PVT)	Peniche (GAM)	Cascais (GUI)	Lisboa (ALG)	Sines (STP)	Aljezur (BOR)
Ts	2900	580	1900	4700	610	n.a.	1500	1400	1400
Tm	3600	540	1900	5100	500	n.a.	1500	1400	1500
C29 17 $\alpha$	14000	2100	7200	17000	2000	n.a.	7000	7400	5600
C29 18 $\alpha$	3000	700	2000	3500	770	n.a.	1900	2300	1800
C29 17 $\beta$	1300	290	720	1200	170	n.a.	530	740	770
Oleanane	1100	610	750	1300	290	n.a.	1700	1500	2300
C30 17 $\alpha$	6700	1600	5300	7800	1400	n.a.	3400	4700	470
C30 17 $\beta$	900	310	490	980	150	n.a.	610	590	690
C31 S	7500	1100	4200	6800	1400	n.a.	3900	4700	2900
C31 R	5700	n.a.	3200	5200	1000	n.a.	3100	3400	2200
C32 S	4100	n.a.	2400	4100	890	n.a.	2200	2500	1600
C32 R	3000	n.a.	1600	2700	580	n.a.	1500	1900	1100
C33 S	2300	n.a.	1300	2800	540	n.a.	1300	1800	960
C33 R	1800	220	840	1800	320	n.a.	950	1300	670
C34 S	1400	200	720	1600	290	n.a.	760	1100	530
C34 R	980	n.a.	490	1100	200	n.a.	780	780	370
C35 S	1100	n.a.	780	1800	340	n.a.	1500	1000	500
C35 R	660	n.a.	540	1100	150	n.a.	800	730	320
Total Hopanes (ng/g)	62000	8300	37000	71000	12000	n.a.	35000	39000	30000
Total Hopanes ( $\mu$ g/g)	62	8.3	37	71	12	n.a.	35	39	30
C31-35/C30	4.3	0.91	3.0	3.7	4.1	n.a.	5.0	4.1	2.4
C29/C30	2.1	1.3	1.4	2.2	1.4	n.a.	2.1	1.6	1.2
Oleanane/C30	0.17	0.37	0.14	0.16	0.21	n.a.	0.50	0.32	0.48
Tm/Ts	1.3	0.93	1.0	1.1	0.81	n.a.	1.0	1.0	1.1

n.a. = not analyzed.

p,p'-DDE, and 0.1% o,p'-DDE (IPCS, 1979). Recently, a new source of DDT pollution has emerged with the use of dicofol as an antifouling agent (Qiu et al., 2004). In the case of pollution by dicofol, Qiu et al. (2004) suggested that o,p'-DDT would predominate over p,p'-DDT. However, no predominance of o,p'-DDT was observed in the pres-

ent study, indicating that the DDTs in the present study did not come from dicofol but from pesticides used in agricultural activity. Though Porto and Lisboa are urbanized areas, they are located at the mouths of large rivers (the Douro and Tejo Rivers, respectively), and may receive contaminants from the river catchments. Thus,



use of DDTs as pesticides in the catchments may be the reason for the higher concentrations of DDTs in the two locations. Because DDT predominated over its degradation products (DDD and DDE) at most of the locations, including Porto and Lisboa, current usage (and/or inputs) of the pesticide DDT is suggested, although its agricultural use was banned by the Stockholm convention as part of UNEP (2001). On the other hand, HCH concentrations in the pellets were lower than the LOQ ( $<1$  ng/g-pellet) at most of the locations in Portugal (Table 2). In pellets from Aljezur, significant concentrations of HCHs were detected. However, the HCH concentrations at Aljezur (3 ng/g-pellet) were also close to the LOQ. Octanol–water partition coefficients ( $K_{ow}$ ) for HCHs ( $\log K_{ow}$  of  $\gamma$ -HCH: 3.8) are lower than those for PCBs and DDTs (4.46–8.18, 5.87–6.91, respectively) and, therefore, less partitioning of HCHs into pellets could be responsible for the lower concentrations of HCHs in the pellet samples. However, a more likely reason for the lower HCH concentrations is higher vapor pressure of  $\alpha$  and  $\gamma$  HCHs compared with those of middle and high chlorinated PCBs and DDTs (Hinckley et al., 1990) which facilitates evaporation of HCHs from seawater to the atmosphere. This non- or trace-detection of HCHs is consistent with that in many locations in the world (Ogata et al., 2009), and indicates the effectiveness of the Stockholm convention, which banned the use of HCH pesticides as part of UNEP (2009). Table 3 shows the PAH concentrations in pellets from Portuguese beaches. In all the locations, except for Sines, PAH concentrations (sum of 33 analytes) ranged from  $\sim 50$  ng/g to 400 ng/g-pellet. These concentrations were close to the LOQ and comparable to those in Karapanagioti et al. (2011) and Van et al. (2012). We calculated the following ratios as indicators of the source of PAHs: methyl phenanthrene/phenanthrene (MP/P ratio) methyl pyrene/pyrene (MPy/Py ratio), methyl chrysene/chrysene (MC/C) and methyl PAHs/PAHs (MPAHs/PAHs). In most of the samples, methylated PAHs were depleted, with lower MP/P ratios (ranging from 0.5 to 0.9), indicating that pyrogenic PAHs were predominant. However, two orders of magnitude higher concentrations of PAHs (24,300 ng/g-pellet) were detected in the pellet sample from Sines, which exhibited a pronounced petrogenic signature (MP/P ratio of 4.5), indicating exclusive petrogenic pollution according to Saha et al. (2012). Therefore, there must be a local petrogenic source (or sources) in the vicinity of Sines. Near the sampling site in Sines, which is a small city in rural landscape, there is a large oil and gas electric power plant, which could be one source. Because lower molecular weight species were predominant and higher molecular weight species were depleted in the sample from Sines, no indication of sources was obtained from the MPy/Py or MC/C ratios. PAHs, especially MP/P ratios, could be useful as markers of petroleum pollution. However, pellets are exposed to sunlight while on the beach and/or floating on the sea surface, and therefore the disappearance of PAH species and the alteration of PAH profiles are likely. More observations are necessary to evaluate the utility of PAHs as markers of petroleum pollution.

Hopanes were detected in all locations (Table 4). Hopane concentrations in the pellet samples ranged from 8250 ng/g to 70,800 ng/g-pellet, and their spatial variation among the locations was less than that of PCBs, DDTs, and PAHs. The ratio of maximum to minimum was 9 for hopanes versus 29 for PCBs, 30 for DDTs, and 490 for PAHs. This relatively homogeneous distribution of hopanes could be due to ubiquitous and continuous inputs from automobiles, ships, and other anthropogenic activities, and to the persistent nature of hopanes. The relatively high concentrations of hopanes at Porto (61,800 ng/g-pellet) and Lisboa (3500 ng/g-pellet) can be explained by anthropogenic inputs from the urbanized areas. However, similar levels of hopanes were observed in remote areas such as Leiria, Sines, and Aljezur. Hopane concentrations were not consistent with those of PAHs; extremely high concentrations of hopanes were not detected in the pellet sample from Sines,

for example, although extremely high concentrations of PAHs, with an exclusive petrogenic signature, were observed in the same sample, suggesting that some petrogenic source not containing hopanes, such as diesel oil or gasoline, may have contributed to the Sines results.

Hopane composition varies depending on the origin of the crude oil, and can be used for source identification of oil pollution (Zakaria et al., 2000,2001). Hopane in the pellets from the Portuguese coast was relatively uniform,  $C_{29}17\alpha$  predominated over  $C_{30}17\alpha$ , and homohopanes (ranging from  $C_{31}$  to  $C_{35}$ ) were relatively abundant. This hopane profile is similar to crude oil from the Middle East (Fig. 5). Typically, Middle East crude oil is used as lubricating oil due to its less viscous nature. The hopane compositions in the pellets in the present study suggest that the hopanes were derived from lubricating oil. For more detailed source identification of the respective petroleum inputs (e.g., used engine oil from automobiles or ships), specific source materials should be analyzed in future study.

Analysis of pellets from nine locations along 700 km of the Portuguese Atlantic coast demonstrated spatial patterns of PCBs, DDTs, HCHs, PAHs, and hopanes. Their composition and the spatial pattern of their concentrations provided information on the sources and behavior of organic micropollutants on the Portuguese coast. The present study demonstrated that multiple locations, including locations in both urbanized and remote areas, must be

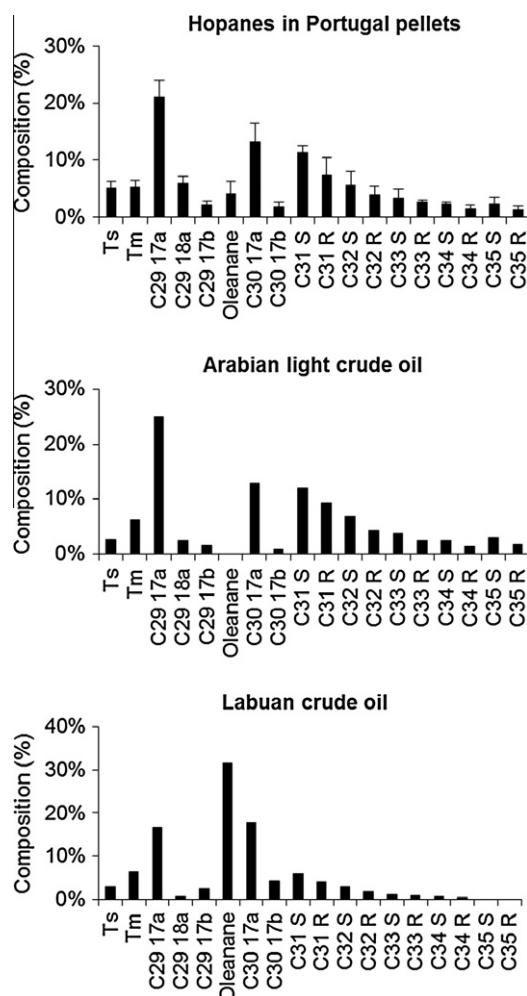


Fig. 5. Hopane compositions in pellets from eight Portuguese beaches (arithmetic mean), Arabian light crude oil (Middle East)\* and Labuan crude oil (South-Eastern Asia)\*. \*Data on the crude oil were cited from Zakaria et al. (2000) with modification due to increased number of hopane standard available.

sampled to properly determine the pollution status of respective countries and the behavior of pollutants in these countries. A combination of PAH and hopane analysis may offer a useful approach for monitoring petroleum pollution by the International Pellet Watch. More studies are necessary to understand the background levels of hopanes in pellets, and the persistence of PAHs in pellets, in marine environments.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2013.02.008>.

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